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Oxidative Addition of Group 13 and 14 Metal Halides and Alkyls to Ga(DDP) (DDP = Bulky Bisimidinate)

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The oxidative addition of a variety of group 13 and group 14 halides and alkyls R_aMX to the mono valent group 13 bis-imidinate Ga(DDP) (DDP = 2-{(2,6-diisopropyl-phenyl)amino}−4-{(2,6-diisopropylphenyl)imino}−2-pentene) is reported. Accordingly, the insertion of Ga(DDP) into the Ga-Me bond of $GaMe_3$ yield in the complexes [{(DDP)GaMe}$GaMe_2$] (**1**) and [{(DDP)GaMe}$_2$GaMe] (**2**), respectively, which show a temperature-dependent equilibrium between **1** at higher temperatures and **2** at lower temperatures. In the case of $GaCl_3$, the only isolable product is [{(DDP)GaCl}$_2$GaCl] (**3**). The related reaction of $SnMe_2Cl_2$ with Ga(DDP) yields the compound [Me$_2$Sn{ClGa(DDP)}$_2$] (**4**), whereas $SnMe_4$ behaves inert. In the case of $SiCl_4$, only the monoinsertion product [Cl$_3$Si{ClGa(DDP)}] (**5**) was observed. Finally, [(CH$_3$)$_3$C{ClGa(DDP)}] (**6**) is synthesized by insertion of Ga(DDP) into the C−Cl bond of ClC(CH$_3$)$_3$. All new compounds were fully characterized by elemental analysis, NMR-spectroscopy, and single-crystal X-ray diffraction analysis.

Introduction

The chemistry of monovalent group 13 compounds ER is a fascinating part of modern inorganic chemistry and has been explored extensively in the past 20 years.[1–14] Their coordination chemistry to electron-rich transition metals is very rich, especially for R = Cp*, ranging from classical organometallic reactions such as C−H or C−C bond activation reactions,[15–17] to unprecedented product classes, for example, homoleptic cluster compounds of the type $M_a(ER)_b$.[18–20] Quite recently, Power, Roesky, and Hill added a new class of compounds to the series ER, that is the bulky bisimidinates E(DDP) (DDP = 2-{(2,6-diisopropyl-phenyl)amino}−4-{(2,6-diisopropylphenyl)imino}−2-pentene).[21–23] Additionally, the related borylene complex [B{ArNCH}$_2$]Li was reported by Segawa et al. in 2006.[24] The chemistry of these compounds has proven to be very prosperous and especially in the case of Al(DDP) a variety of coordination, oxidation and insertion reactions were studied in some detail.[25–28] Thus, the aluminum center in Al(DDP) has been shown to be rather Lewis acidic,

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Scheme 1. Synthesis of [{(DDP)GaMe}GaMe₂] (**1**) and [{(DDP)GaMe}₂GaX] (X = Me (**2**), Cl (**3**))
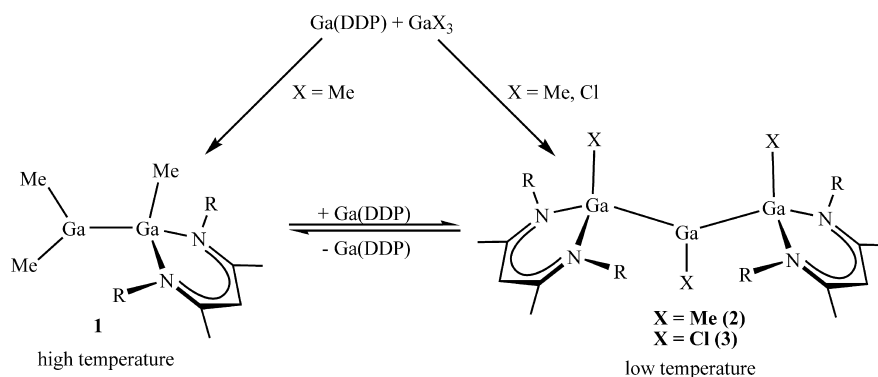
coordinating also weak donors such as the aromatic $C-F$ group of a $B(C_6F_5)_3$ moiety.[29] Also, acetylene is coordinating strongly to the aluminum center leading to a metallacyclo-propene structure through backbonding of Al(I) to the coordinating acetylene.[30] Al(DDP) is easily oxidized by a variety of reagents, P_4 or S_8 for example, leading to the dimeric aluminacycles [(DDP)Al]₂P₄[31] and [(DDP)Al]₂S₆.[32] In the case of Ga(DDP), the latter reaction leads to the dimeric sulfide [(DDP)Ga]₂S, whereas oxidation of Ga(DDP) by N_2O leads to the structurally analogous oxide.[33]

Whereas the chemistry of the neutral compounds E(DDP) is mainly studied in the context of nonmetallic main group element substrates as outlined above, the anionic NHC congener [Ga{[N(Ar)C(H)]₂}]⁻ (Ar = 2,6-^{i}Pr₂C₆H₃) has been shown to form very stable bonds to electropositive elements such as Ca, Mg, Nd, Pb, Ge, or Sn.[34–36] In many cases, these compounds are prepared by salt metathesis reactions of substrates containing M−X bonds, which on reaction with [K(tmeda)][Ga{[N(Ar)C(H)]₂}] lead to M−Ga complexes under elimination of KX. The anionic intermediates of these reactions, that is the initial products formed by coordination or oxidative addition of M−X to the gallium heterocycle, have not been reported so far. However, the general possibility for oxidative addition of group 14 elements to gallium(I) heterocycles has been reported by Jones et al.[37,38]

Against this background of previous work, we became interested in the coordination behavior of Ga(DDP) to

electropositive main group element halides and alkyls. The fact that the Ga(I) center in this compound is easily oxidized suggests the use of substrates, which are intrinsically more difficult to reduce, such as Ga(III), Si(IV), or Sn(IV). In fact, the rich redox chemistry of Ga(DDP) could be an entry into M−Ga compounds also of the more electropositive main group metals, in analogy to the insertion reactions of Ga(DDP) into transition-metal halide bonds, which has been studied by us and others in more detail.[39–41] In this article, we present the reactions of Ga(DDP) with GaMe₃, GaCl₃, SiCl₄, ClC(CH₃)₃, and Me₂SnCl₂. In all cases, oxidative addition of M−X to Ga(DDP) is observed, leading to a variety of new main group metal−gallium compounds.

Results and Discussion

Oxidative Addition of GaR₃ (R = CH₃, Cl) to Ga(DDP). When adding 1 equiv of GaMe₃ (as a 0.25 M solution in hexane) to a yellow solution of Ga(DDP) in hexane under vigorous stirring, the color of the solution turns to intense yellow. On storing, the resulting mixture at −30 °C overnight, bright-yellow crystals of [{(DDP)GaMe}Ga-Me₂] (**1**) can be obtained in 81% yield (Scheme 1). **1** is quite air sensitive but stable in an inert gas atmosphere for several days and can be dissolved in non polar organic solvents such as hexane or toluene.

The ¹H NMR spectrum of **1** in C₆D₆ at room temperature shows the typical set of signals for a Ga(DDP) moiety with reduced (C_S) symmetry, which is a result of the insertion of Ga(DDP) in one Ga−Me bond of GaMe₃ and is known for the insertion into transition-metal halide bonds (e.g., in [(Ph₃P)AuCl] and [(COE)₂RhCl]₂).[39,40] Additionally, signals at 0.37 ppm (6H) and −0.25 ppm (3H) can be assigned to the methyl protons of the GaMe₂ moiety and the GaMe(DDP) ligand, respectively. The ¹³C NMR spectrum is in good agreement with this result, showing two distinct signals for {MeGa(DDP)} (1.4 ppm) and {GaMe₂} (−6.1 ppm), respectively.

Single crystals for X-ray diffraction could be obtained from a saturated solution of **1** in hexane at −30 °C. The molecular structure of **1** is shown in Figure 1 (left).

1 consists of a gallium atom, which is coordinated in a trigonal-planar geometry by two methyl and one {(DDP)-

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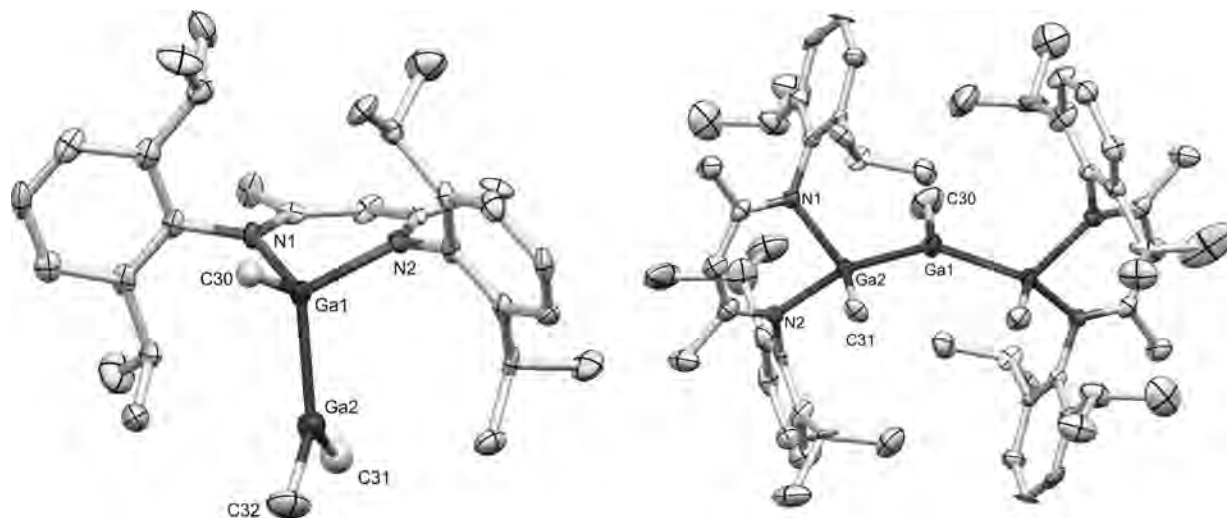
Figure 1. Molecular structure of [{(DDP)GaMe}GaMe₂] (**1**) (left) and [{(DDP)GaMe}₂GaMe] (**2**) (right). Selected bond length (angstroms) and angles (degrees) for **1**: Ga1−Ga2 2.4508(18), Ga1−N1 1.981(5), Ga1−N2 2.001(6), Ga1−C30 1.981(6), Ga2−C31 1.815(7), Ga2−C32 1.990(7); N1−Ga1−N2 93.0(2), C30−Ga1−Ga2 113.8(2), C31−Ga2−Ga1 121.8(3), C32−Ga2−Ga1 121.2(2), C31−Ga2−C32 116.9(4), C30−Ga1−Ga2-C3 22.5. Selected bond length (angstroms) and angles (degrees) for **2**: Ga1−Ga2 2.5030(18), Ga1−Ga2* 2.5062(17), Ga2−N1 2.006(8), Ga2−N2 2.005(8), Ga2*−N1 2.048(8), Ga2*−N2 2.037(7), Ga1−C30 2.000(9), Ga2−C31 1.981(7), Ga2*−C3* 1.996(7); Ga2−Ga1−Ga2* 138.37(5), C30−Ga1−Ga2 122.5(3), C31−Ga1−Ga2* 124.7(3), C31−Ga2−Ga1 112.2(2), C31*−Ga2*−Ga1 121.0(2), N1−Ga1−N2 91.7(3), N1−Ga2−N2 92.1(3), C30−Ga1−Ga2−C31 179.8(4), C31−Ga2−Ga2*−C31* 0.08.

GaMe} ligand, respectively. The Ga−Ga bond distance (2.4508(18) Å) is comparable to other covalent Ga−Ga interactions such as [Cp*Ga(GaCp*Cl₂)] (2.4245(3) Å)[42] or [{(CSiMe₃)GaBr}₂] (2.43 Å).[43]

Interestingly, the Ga−C bond length of the methyl groups cis to each other are quite similar with 1.981(6) Å (Ga1−C30) and 1.990(7) Å (Ga2−C32) and thus is comparable to those in [(DDP)GaMe₂] (1.970(2) and 1.979(2) Å)[44] or [(DDP)GaMeCl] (1.956(2) Å),[45] respectively. In contrast, the bond length of the methyl group cis to the DDP backbone is distinctly shorter (Ga2−C31: 1.815(7) Å). However, similar bond distances can be found for example in [(Me₃Ga)₄-(C₆N₄)] (1.837 Å; C₆N₄ = hexamethylenetetramine, N₄, adamantane).[46]

The insertion of the Ga(DDP) moiety into the Ga−Me bond is reflected by the distorted tetrahedral geometry at the gallium center, coordinated by the DDP-backbone, the methyl, and the GaMe₂ moiety, respectively (angular sum Ga−N−N−Me: 319.55), with a dihedral angle between the C₃N₂ and the GaN₂ arrays of 25.67°. The Ga−N bond distances are 1.981(5) Å and 2.001(6) Å, which is consistent with an electron rich gallium center. Similar Ga−N bond distances can be found for example in [{(DDP)Ga}-Au{Ga(DDP)Cl}] (1.936(5)−1.995(5) Å)[39] or [(coe)(η⁶-benzene)Rh{(DDP)GaCl}] (1.974(3) Å and 2.018(3) Å).

On slow addition of GaMe₃ to 2 equiv of Ga(DDP) in hexane, the color changes to orange after the addition is completed. Stirring the reaction mixture for 1 h at room temperature and cooling it to −30 °C overnight leads to a mixture of bright-yellow single crystals of **1** (as proven by single-crystal X-ray diffraction analysis) and deep-orange crystals of [{(DDP)GaMe}₂GaMe] (**2**) (Scheme 1). The overall yield of **2** is rather low (22−25%) and could only be determined by manual separation of the crystals. **2** is stable in the solid state in an inert gas atmosphere for several days without decomposition, but readily dissociates to **1** and Ga(DDP) on redissolving in all common organic solvents at room temperature, as proven by ¹H NMR spectroscopy. Therefore, variable-temperature ¹H NMR spectroscopy of a 2:1 mixture of Ga(DDP) and Me₃Ga in toluene was performed (Supporting Information).

At 50 °C, only signals for free Ga(DDP) (5.18 ppm) and **1** (4.83 ppm) are observed. On cooling the solution to room temperature, new signals at 4.74, 0.42, and −0.01 ppm appear, which can be assigned to the γ-CH of the DDP backbone and the two distinct GaMe groups of **2**. On further cooling the solution to −40 °C, the signals for free Ga(DDP) and **1** vanish, and only the signals for **2** remain. Thus, a temperature-dependent equilibrium between **2**, **1**, and Ga(DDP) exists, which is shifted toward **2** at lower temperature (Scheme 1).

2 crystallizes in the triclinic space group P1̄ with half of the molecule in the unit cell. Figure 1 (right) shows the molecular structure of **2**, which consists of a central GaMe moiety, which is coordinated by a methyl and two {(DDP)-GaMe} moieties in a trigonal planar geometry (angular sum Ga−Ga−Ga−Me: 360.0°). The two Ga−Ga bonds of 2.5030(18) and 2.5062(17) Å are slightly longer than in **1** (2.4508(18)) but within the range of Ga−Ga distances in other trigallanes (e.g., 2.451(1) and 2.460(1) Å in [{(PEt₃)-

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Table 1. Crystallographic Data for **1–6**

	1	2	3	4	5	6
empirical formula	$C_{32}H_{50}Ga_2N_2$	$C_{59}H_{85}Ga_3N_4$	$C_{58}H_{82}Cl_3Ga_3N_4$	$C_{60}H_{88}Cl_2Ga_2N_4Sn$	$C_{29}H_{41}Cl_4GaN_2Si$	$C_{33}H_{50}ClGaN_2$
fw	602.18	1059.47	1150.83	1197.43	657.25	579.92
temperature [K]	105(2)	113(2)	113(2)	113(2)	113(2)	113(2)
wavelength [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	triclinic	Triclinic	Monoclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/m$	$P2_1/c$
a (Å)	11.025(5)	8.957(5)	14.5470(14)	22.3307(10)	9.0848(5)	10.203(12)
b (Å)	12.214(5)	12.996(12)	20.3303(18)	12.8162(5)	20.4648(15)	26.884(8)
c (Å)	14.119(6)	14.388(7)	24.2913(14)	32.5680(18)	9.6349(6)	13.510(12)
α (deg)	65.03(4)	85.47(6)	90.00	90.00	90.00	90.00
β (deg)	68.78(4)	80.28(5)	104.506(7)	118.894(4)	114.738(6)	120.31(6)
γ (deg)	70.49(4)	80.24(6)	90.00	90.00	90.00	90.00
V (Å^3)	1569.3(12)	1625(2)	6955.0(10)	8160.5(7)	1626.92(18)	3199(5)
Z	2	1	2	4	2	2
δ_{calcd} [g cm^{-3}]	1.274	1.083	1.273	1.047	1.342	1.204
μ [mm^{-1}]	1.738	1.269	1.311	1.058	1.232	0.966
F (000)	636	623	2800	2688	684	1240
2θ range [deg]	3.05 – 27.56	3.36 – 27.56	2.71 – 27.58	2.62 – 27.59	2.66 – 27.58	3.08 – 25.10
	$-14 \leq h \leq 10$	$-11 \leq h \leq 10$	$-18 \leq h \leq 18$	$-24 \leq h \leq 29$	$-10 \leq h \leq 11$	$-9 \leq h \leq 12$
index ranges	$-15 \leq k \leq 15$	$-16 \leq k \leq 16$	$-25 \leq k \leq 26$	$-16 \leq k \leq 24$	$-23 \leq k \leq 26$	$-30 \leq k \leq 31$
	$-18 \leq l \leq 16$	$-18 \leq l \leq 18$	$-24 \leq l \leq 31$	$-14 \leq l \leq 42$	$-12 \leq l \leq 11$	$-16 \leq l \leq 16$
reflns collected	7148	7417	15 967	18 841	3867	5641
reflns unique	2275	4517	3569	6188	2754	4233
GOF on F^2	0.751	1.016	0.478	0.721	0.983	1.163
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0667$	$R_1 = 0.0637$	$R_1 = 0.0436$	$R_1 = 0.0466$	$R_1 = 0.0451$	$R_1 = 0.0642$
	$wR_2 = 0.0966$	$wR_2 = 0.1635$	$wR_2 = 0.527$	$wR_2 = 0.1156$	$wR_2 = 0.1214$	$wR_2 = 0.1060$
R indices (all data)	$R_1 = 0.2123,$	$R_1 = 0.0996,$	$R_1 = 0.02155,$	$R_1 = 0.1276,$	$R_1 = 0.0662,$	$R_1 = 0.0868,$
	$wR_2 = 0.1300$	$wR_2 = 0.1754$	$wR_2 = 0.678$	$wR_2 = 0.1254$	$wR_2 = 0.1377$	$wR_2 = 0.1120$

GaI$_2$}$_2$Ga(I)(PEt$_3$)],[47] 2.4071(9) Å in [GaH2(Ga{NC(R)C-(H)}2)2][K(tmeda)][48] or 2.5267(7) and 2.879(1) in [(^{t}Bu$_3$Si)$_4$Ga$_3$][49]). The gallium atoms and the methyl groups are coplanar (torsion angles 0.20° and 0.24°) and coordinated trans to each other, giving a Y-shaped arrangement (Ga–Ga–Ga angle: 138.37°).

The DDP backbones are both orientated perpendicular toward the GaMe plane. Obviously due to steric interactions, only one (DDP)Ga ring is planar (Ga1), whereas in the second one the GaN$_2$ and C$_3$N$_2$ planes adopt an angle of 35.7°. This tilting is within the range of other sterically crowded Ga(DDP) complexes, for example [{(DDP)Ga}Au-{Ga(DDP)Cl}] (22.4°)[39] or [(COE)(η^6-benzene)Rh{(DDP)-GaCl}] (29.8°). The Ga–N bond distances in **2** (2.005(8) Å to 2.048(8) Å) are slightly longer than those in **1** (1.981(5) Å and 2.001(6) Å).

By using GaCl$_3$ instead of GaMe$_3$, the only isolable product is [{(DDP)GaCl}$_2$GaCl] (**3**), independent of the reaction conditions or the ratio of the reactants used (Scheme 1). **3** is soluble in common organic solvents and can be stored without decomposition in an inert gas atmosphere for several weeks. The ^{1}H NMR spectrum of **3** in C$_6$D$_6$ at room temperature does not show the expected splitting of the DDP-proton signals for a C_s symmetric DDP-ligand; instead only one septet signal at 3.43 ppm as well as two doublet signals at 1.42 and 1.10 ppm can be observed, indicating a fast exchange of the chlorine atoms in solution. Additionally, the ^{13}C NMR spectrum is in good agreement with this result.

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Crystals suitable for single-crystal X-ray analysis could be grown from a saturated solution of **3** in hexane at −30 °C overnight. The molecular structure is similar to that of **2** with chlorine atoms instead of methyl groups coordinating the gallium centers. A mercury plot as well as a table with selected bond lengths and angles can be found in the Supporting Information. The Ga–Ga bond distances of 2.4376(7) Å and 2.4436(8) Å are shorter than those in **2**, but still in the range of Ga$_3$ chains known in literature (vide supra). The distinctly shorter Ga–N bond distances of **3** (1.929(4) to 1.948(4) Å) as compared to **2** (2.005(8) Å to 2.048(8) Å) are explained by the substantial polarization and thus enhanced electrophilicity of the gallium centers caused by the chloride ligands.

On reaction of AlMe$_3$ with Ga(DDP) in toluene, no oxidative addition reaction can be observed. Instead, single crystals of pure ligand can be isolated when cooling the reaction mixture. However, the ^{1}H NMR spectrum of the reaction mixture shows a clear shift of the resonances for free Ga(DDP), indicating the formation of a donor–acceptor bond between Ga(DDP) and AlMe$_3$. However, all attempts to grow single crystals of this adduct failed.

Oxidative Addition of Group 14 halides R$_3$ECl (E = C, Si, Sn) to Ga(DDP). Ga(DDP) readily reacts with [SnMe$_2$Cl$_2$] in hexane at room temperature, giving [Me$_2$Sn-{ClGa(DDP)}$_2$] (**4**) as colorless crystals after crystallization from hexane at −30° (Scheme 2). **4** readily dissolves in all common organic solvents such as hexane or THF and can be stored in an inert gas atmosphere for several days, whereas immediate decomposition occurs upon contact with air. The reaction of less than 2 equiv Ga(DDP) with [SnMe$_2$Cl$_2$] only reduces the yield of **4** and does not lead to different products. Interestingly, only the insertion into the Sn–Cl bonds of

Scheme 2. Synthesis of [Me$_2$Sn{ClGa(DDP)}$_2$] (**4**)
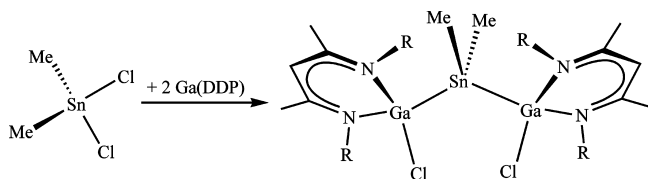
SnMe$_2$Cl$_2$ occurs, probably because of kinetic reasons. It should be noted, that SnMe$_4$ behaves inert against Ga(DDP) and no reaction is observed as indicated by ^{119}Sn NMR spectroscopy.

The ^{1}H NMR spectrum of **4** at room temperature shows signals for a Ga(DDP) ligand with C_s symmetry. The signal for the protons of the SnMe$_2$ moiety can be found at −0.76 ppm, showing the expected ^{119}Sn satellites with a coupling constant of 21.7 Hz. The ^{119}Sn-NMR spectrum shows a resonance at 1189 ppm relative to SnMe$_4$. This large downfield-shift compared to the resonances for the Sn−Ga complexes [K(tmeda)][Sn{CH(SiMe$_3$)$_2$}$_2$Ga{[N(Ar)C-(H)]$_2$}]$^-$ ($\delta = −97.9$ ppm) and [K(tmeda)][(Ar′)$_2$SnGa{[N(Ar)-C(H)]$_2$}]$^-$ (Ar′ = C$_6$H$_2$Pr$^i_3$−2,4,6; $\delta = −306.7$ ppm) is not surprising considering the anionic nature of the latter complexes, which can be compared to trialkyl stannate anions (e.g., LiSnMe$_3$; $\delta = −189$ ppm).[50] Comparable shifts to **4** are reported for the neutral complexes [((Giso)SnGa-{[N(Ar)C(H)]$_2$}] ($\delta = 455$ ppm; Giso = [Pr$^i_2$NC{N(Ar)}$_2$]$^-$) or the related NHC complex [(NHC)Sn(Ar′)$_2$] ($\delta = 710$ ppm).[51]

4 crystallizes in the monoclinic space group $P2_1/c$. The molecular structure is depicted in Figure 2 and consists of a central SnMe$_2$ moiety in a distorted tetrahedral coordination environment surrounded by two {ClGa(DDP)} and two methyl groups. The Sn−Ga bond distances are almost identical with 2.6236(7) Å and 2.6328(7) Å, which are significantly shorter than the reported Sn−Ga bond distances in the anionic complexes [R$_2$SnGa{[N(Ar)C(H)]$_2$}]$^-$ (2.7186(6) Å) and [RSn[Ga{[N(Ar)C(H)]$_2$}]$_2$] (2.6361(5) Å and 2.6610(5) Å) (R = CH(SiMe$_3$)$_2$).[36] Also, the neutral complex [((Giso)SnGa{[N(Ar)C(H)]$_2$}] exhibits longer bond distances (2.6888(6) Å). The distorted tetrahedral coordination environment at the tin center is reflected in a comparably large Ga−Sn−Ga bond angle of 127° and a rather small angle of 103° for the Me−Sn−Me arrangement. The gallium centers of the Ga(DDP) ligands are also tetrahedrally coordinated by the nitrogen atoms of the DDP backbone, the tin and the chlorine atoms, leading to dihedral angles between the C$_3$N$_2$ and the GaN$_2$ arrays of 35.87° (Ga1) and 23.34° (Ga2), respectively. The Ga−Cl bond distances (av. 2.247 Å) are similar to those in [(DDP)GaCl$_2$] (2.228(1) Å and 2.218(1) Å)[44] but slightly shorter than in [(COE)(η^6-benzene)-Rh{(DDP)GaCl}] (2.321(2) Å).[40]

Upon mixing Ga(DDP) with SiCl$_4$ in a ratio of 1:1 in hexane or toluene (Scheme 3), a colorless precipitate is formed. On recrystallization, colorless crystals of [Cl$_3$Si-

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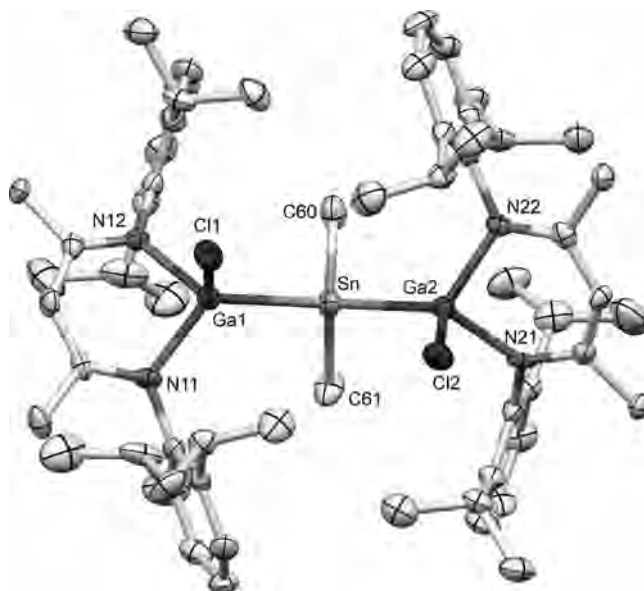
Figure 2. Molecular structure of [Me$_2$Sn{ClGa(DDP)}$_2$] (**4**). Selected bond lengths (angstroms) and angles (degrees); Sn−C60 2.175(5), Sn−C61 2.178(5), Sn−Ga1 2.6236(7), Sn−Ga2 2.6328(7), Ga1−Cl1 2.2471(15), Ga2−Cl2 2.2470(15), Ga1−N11 1.977(4), Ga1−N12 1.969(4), Ga2−N21 1.979(4), Ga2−N2 1.962(4); C60−Sn−C61 103.4(2), Ga1−Sn−Ga21 21.27(2), N11−Ga1−N1294.14(18), N21−Ga2−N2294.78(18), Sn−Ga1−Cl11 15.77(4), Sn−Ga2−Cl2 116.72(4).
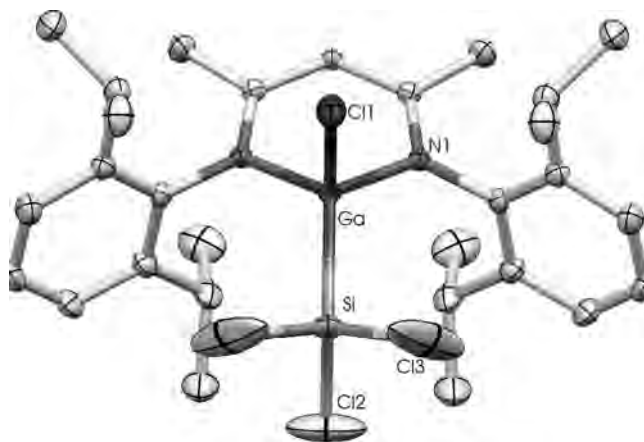
Figure 3. Molecular structure of [Cl$_3$Si{ClGa(DDP)}] (**5**). Selected bond lengths (angstroms) and angles (degrees): Ga−Si 2.3860(13), Si−Cl2 1.999(2), Si−Cl3 2.0135(15), Ga−N1 1.917(2), Ga−Cl1 2.1980(11); N1−Ga−N1* 98.46(14), Cl1−Ga−Si 103.71(5), Cl2−Si−Cl3 105.75(8), Cl3−Si−Cl3 105.04(16), Cl2−Si−Ga 121.80(8).

Scheme 3. Synthesis of [Cl$_3$Si{ClGa(DDP)}] (**5**)
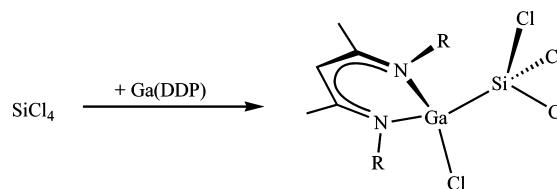
{ClGa(DDP)}] (**5**) are obtained in high yields. It should be noted that the 1:1 reaction product **5** is formed also in the presence of excess of Ga(DDP). **5** is soluble in several organic solvents (hexane, toluene, benzene) and stable at room temperature in an inert gas atmosphere for several weeks without decomposition (Figure 3).

Figure 4. Molecular structure of [(DDP)Ga(tBu)(Cl)] (**6**). Selected bond lengths (angstroms) and angles (degrees): Ga1−N1 1.943(6), Ga1−N2 1.956(6), Ga1−Cl 2.251(2), Ga1−C30 2.029(8), Ga1−C31 1.997(7), N3−C30 1.141(9); N1−Ga1−N2 95.4(2), N1−Ga1−C30 102.1(3), N1−Ga1−C31 122.4(3), N2−Ga1−C30 101.8(3), N2−Ga1−C31 121.5(3), C31−Ga1−C30 110.3(3).

Scheme 4. Synthesis of [{(DDP)Ga}(^{t}Bu)Cl] (**6**)

^{1}H NMR and ^{13}C NMR spectra are in good agreement with the solid-state structure described below and will not be discussed here in more detail.

5 crystallizes in the monoclinic space group $P2_1/m$. The gallium center is coordinated in a distorted tetrahedral geometry and lies significantly above the C_3N_2 plane (0.639Å), causing a dihedral angle of 30.13°. The Ga−Cl bond length of 2.1980(11) Å is shorter than those in [(DDP)GaCl$_2$] (2.228(1) Å and 2.218(1) Å)[44] but well within the range for other Ga−Cl bond distances reported in literature. The Ga−Si bond length of 2.3860(13) Å is significantly shorter than that in the Ga(I) tetramer [{(^{t}Bu$_3$Si)Ga}$_4$] (2.45 Å)[52] or the Ga(III) dihalide [(^{t}Bu$_3$Si)GaCl$_2$(THF)] (2.42 Å).[53] Similar bond distances are reported for example for the dimeric compound [{(Me$_3$Si)$_3$-SiGaMeCl}$_2$].[54]

Whereas no reaction of Ga(DDP) is observed in the presence of fluorobenzene or chlorobenzene, decomposition and undefined products are obtained with CH$_2$Cl$_2$ and CHCl$_3$. In contrast to that, the reaction of Ga(DDP) with ^{t}BuCl yields [{(DDP)Ga}(^{t}Bu)Cl] (**6**) as colorless crystals (Scheme 4).

The ^{1}H NMR and ^{13}C spectra of **6** in C$_6$D$_6$ at room temperature show the expected signals for a DDP-moiety with reduced (C_s) symmetry and will not be discussed here in more detail.

The molecular structure of **6** (Figure 4) consists of a distorted tetrahedrally coordinated gallium center with a

Ga−C$_{tBu}$ bond distance very similar to that in [(^{t}Bu){Ga-(DDP)}(CN)] (1.994(5) Å).[55] The Ga−Cl bond distance (2.251(2) Å) is slightly longer than in [(DDP)Ga(Me)Cl] (2.223(1) Å) or [Cl$_3$Si{ClGa(DDP)}] (**5**, 2.1980(11) Å). The Ga−N bond distances (1.953(4) Å and 1.965(3) Å) are significantly longer than in [(DDP)GaCl$_2$] (1.906(3) Å and 1.926(3) Å)[44] or **5** (1.962(4)−1.979(4) Å).

Conclusion

In this article, we have shown that oxidative addition of a variety of group 13 and group 14 halides and alkyls is a suitable way for the preparation of compounds with metal−gallium bonds. Thus, the insertion into the Ga−Me bond of GaMe$_3$ yield in the complexes [{(DDP)GaMe}-GaMe$_2$] (**1**) and [{(DDP)GaMe}$_2$GaMe] (**2**), respectively, which show a temperature-dependent equilibrium between **1** (at higher temperatures) and **2** (at lower temperatures). In the case of GaCl$_3$, the only isolable product is [{(DDP)-GaCl}$_2$GaCl] (**3**). In accordance to that, the reaction of [SnMe$_2$Cl$_2$] with Ga(DDP) yields the compound [Me$_2$Sn-{ClGa(DDP)}$_2$] (**4**). In the related reaction with SiCl$_4$, only a monoinsertion can be observed giving [Cl$_3$Si{ClGa-(DDP)}] (**5**). These results show that oxidative addition of M−X of appropriate precursors to monovalent group 13 fragments can be regarded as a general pathway for the formation of metal complexes featuring a {(DDP)Ga}−M bond also in the case of more electropositive metals.

Experimental Section

Methods and Techniques. All manipulations were carried out in an atmosphere of purified argon using standard Schlenk and glovebox techniques. Hexane and toluene were dried using an mBraun Solvent Purification System. The final H$_2$O content in all solvents was checked by Karl Fischer titration and did not exceed 5 ppm. Ga(DDP)[56] was prepared according to literature methods. GaMe$_3$ (Strem), GaCl$_3$, AlMe$_3$, SiCl$_4$, ^{t}BuCl (Aldrich), and SnMe$_2$Cl$_2$ (Fluka) were used as purchased. Elemental analyses were performed by the Microanalytical Laboratory of the Ruhr-Universität Bochum. NMR spectra were recorded on a Bruker Avance DPX-250 spectrometer (^{1}H, 250.1 MHz; ^{13}C, 62.9 MHz) in C$_6$D$_6$ at 298 K, if not stated otherwise. Chemical shifts are given relative to TMS and were referenced to the solvent resonances as internal standards.

All crystal structures were measured on an Oxford Excalibur 2 diffractometer using Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods using *SHELXS-97* and refined against F^2 on all data by full-matrix least-squares with *SHELXL-97*. CCDC 693184 (**1**), CCDC 693185 (**2**), CCDC 693186 (**3**), CCDC 693187 (**4**), CCDC 693188 (**5**), and CCDC 693189 (**6**) contain the supplementary crystallographic data for this article. These data can be obtain free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223−336−033; or deposit@ccdc.cam.uk).

Synthetic Procedures and Analytical Data. [{(DDP)GaMe}-GaMe$_2$] (**1**). Ga(DDP) (200 mg, 0.41 mmol) was dissolved in 5 mL of hexane at room temperature. A solution of GaMe$_3$ (1.65

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mL, 0.2489 M) in hexane was slowly added. The reaction mixture turned to deep yellow and was stirred for an additional 1 h at room temperature. The solvent was reduced to ca. 2 mL and stored at −30 °C overnight to give deep-yellow crystals of 1 in 200 mg yield (81%). ^{1}H NMR (C$_6$D$_6$, 25 °C): δ 7.15−6.95 (m, 6H), 4.78 (s, 1H, γ -CH), 3.52 (sept, 2H, CH(Me)$_2$), 3.04 (sept, 2H, CH(Me)$_2$), 1.52 (s, 6H, CH$_3$), 1.35 (d, 6H, CH(Me)$_2$), 1.13 (d, 12H, CH(Me)$_2$), 1.08 (d, 6H, CH(Me)$_2$), 0.37 (br, 6H, GaMe$_2$), −0.25 (s, 3H, GaMe). ^{13}C NMR (C$_6$D$_6$, 25 °C): δ 168.0 (CN), 143.7 (CMe), 143.6 (Ar), 142.2 (Ar) 126.6 (Ar), 124.3 (Ar), 124.2 (Ar), 96.2 (γ-C), 28.6 (CHMe$_2$), 25.7 (CHMe$_2$), 24.8 (CMe), 24.6 (CMe), 23.9 (CHMe$_2$). 23.2 (CHMe$_2$), 1.4 (GaMe), −6.1 (GaMe). Elemental Anal. Calcd (found) for C$_{32}$H$_{50}$Ga$_2$N$_2$: C, 63.82 (63.89); H, 8.37 (8.41); N, 4.65 (5.08).

[{(DDP)GaMe}$_2$GaMe] (2). Ga(DDP) (0.031 mmol, 150 mg) was dissolved in 5 mL of hexane at room temperature. On slow addition of 0.49 mL of a 0.2489 M solution of GaMe$_3$ in hexane, the color of the solution turns to intense yellow (after the addition of $^1/_2$ equiv of GaMe$_3$) and changes to orange after the addition was completed. After stirring the reaction mixture for 1 h at room temperature and cooling it to −30 °C overnight, a mixture of bright-yellow and deep-orange crystals were obtained. Separating the orange crystals of **2** manually gave a yield of 29 mg (25%). ^{1}H NMR (C$_6$D$_6$, −40 °C): δ 7.15−6.95 (br, m, 12H), 4.64 (s, 2H, γ-CH), 3.35 (br, sept, 8H, CH(Me)$_2$), 1.41 (br, s, 12H, CH$_3$), 1.09 (br, d, 48H, CH(Me)$_2$), 0.63 (br, 6H, (DDP)GaMe), 0.03 (br, s, 3H, GaMe). ^{13}C NMR (C$_6$D$_6$, −40 °C): δ 169.7 (CN), 146.7 (CMe), 146.4 (CMe), 145.5 (CMe), 145.2 (CMe), 140.1 (Ar), 128.9 (Ar), 126.9 (Ar), 126.7 (Ar), 126.2 (Ar), 98.8 (γ -C), 37.6 (CHMe$_2$), 35.0 (CHMe$_2$), 31.3 (CHMe$_2$), 31.2 (CHMe$_2$), 30,7 (CHMe$_2$), 29.8 (CHMe$_2$), 28.2 (CHMe$_2$), 27.4 (CHMe$_2$), 27.1 (CHMe$_2$), 26.4 (CHMe$_2$), 26.2 (CHMe$_2$), 26.1 (CHMe$_2$), 17.4 (CMe), 14.6 (CMe), 4.1 (GaMe), 0.86 (GaMe). Elemental Anal. Calcd (found) for C$_{61}$H$_{91}$Ga$_3$N$_4$: C, 67.24 (67.24); H, 8.42 (8.37); N, 5.17 (5.41).

[{(DDP)GaCl}$_2$GaCl] (3). Ga(DDP) (0.0205 mmol, 100 mg) and 18 mg GaCl$_3$ (0.01 mmol) were dissolved in 5 mL of hexane at room temperature. After stirring the solution for 15 min, the solvent was concentrated and stored at −30 °C overnight to yield pale-yellow/colorless crystals of **3**. Yield: 71 mg (60%). ^{1}H NMR (C$_6$D$_6$): δ 7.15−7.07 (br, m, 24H), 4.74 (s, 2H, γ-CH), 3.43 (sept, 8H, CH(Me)$_2$), 1.49 (s, 12H, CH$_3$), 1.42 (d, 24H, CH(Me)$_2$), 1.10 (d, 24H, CH(Me)$_2$). ^{13}C NMR (C$_6$D$_6$): δ 174.1 (CN), 144.4 (Ar), 141.2 (Ar), 127.5 (Ar), 99.6 (γ -C), 31.5 (CHMe$_2$), 28.1 (CHMe$_2$), 27.4 (CHMe$_2$), 26.4 (CMe). Elemental Anal Calcd (found) for C$_{58}$H$_{82}$Cl$_3$Ga$_3$N$_4$: C, 60.53 (60.56); H, 7.18 (6.89); N, 4.87 (5.41).

[Me$_2$Sn{ClGa(DDP)}$_2$] (4). [SnMe$_2$Cl$_2$] (0.205 mmol, 45 mg) and 200 mg Ga(DDP) (0.41 mmol) were dissolved in toluene at room temperature. The color of the former yellow solution turns slightly orange after several minutes. Concentrating and cooling

the solution to −30 °C overnight gave **4** as colorless crystals. Yield: 125 mg (86%). ^{1}H NMR (C$_6$D$_6$, RT): δ 7.20 − 6.96 (6H), 4.96 (s, 1H, γ-CH), 3.84 (sept, 2H, CH(Me)$_2$), 3.10 (sept, 2H, CH(Me)$_2$), 1.48 (s, 6H, CH$_3$), 1.31 (d, 6H, CH(Me)$_2$), 1.24 (d, 6H, CH(Me)$_2$), 1.21 (d, 6H, CH(Me)$_2$), 0.93 (d, 6H, CH(Me)$_2$), −0.76 (SnMe J = 21.7 Hz). ^{13}C NMR (C$_6$D$_6$, RT): δ 169.0, 146.5, 142.3, 125.5, 123.4, 99.3, 29.5, 28.7, 28.1, 24.8, 24.2, 24.1, 24.0, −12.4. Elemental Anal. Calcd (found) for C$_{60}$H$_{88}$Cl$_2$Ga$_2$N$_4$Sn: C, 60.33 (60.35); H, 7.43 (7.80); N, 4.69 (4.54).

[Cl$_3$Si{ClGa(DDP)}] (5). Ga(DDP) (0.41 mmol, 200 mg) were dissolved in 5 mL hexane, and an excess of SiCl$_4$ (1 mL) was added via a syringe to the solution. Heating the solution to reflux and stirring for 10 min at room temperature afforded a colorless precipitate. All volatiles were removed in vacuo, the colorless precipitate redissolved in 3 mL hexane, and again heated to reflux and slowly cooled to room temperature to give colorless crystals. Yield: 130 mg (48%). ^{1}H NMR (C$_6$D$_6$, RT): δ 7.16−7.04 (6H), 4.88 (s, 1H, γ-CH), 3.74 (sept, 2H, CH(Me)$_2$), 3.18 (sept, 2H, CH(Me)$_2$), 1.54 (s, 6H, CH$_3$), 1.51 (d, 6H, CH(Me)$_2$), 1.38 (d, 6H, CH(Me)$_2$), 1.18 (d, 6H, CH(Me)$_2$), 0.99 (d, 6H, CH(Me)$_2$). ^{13}C NMR (C$_6$D$_6$, RT): δ 170.9, 145.9, 142.6, 140.2, 126.7, 124.1, 123.6, 98.5, 29.9, 28.2, 26.6, 24.9, 24.5, 23.8, 23.5. Elemental Anal. Calcd (found) for C$_{29}$H$_{41}$Cl$_4$GaN$_2$Si: C, 52.99 (53.75); H, 6.29 (5.89); N, 4.26 (4.00).

[(DDP)Ga(^{t}Bu)(Cl)] (6). Ga(DDP) (220 mg, 0.45 mmol) was dissolved in hexane (10 mL) at room temperature. Excess ^{t}BuCl (1 mL, 1,5 mmol) was added via a syringe. The reaction mixture was heated to 60 °C and stirred for 20 min. All volatiles were removed in vacuo and the crude product recrystallized from hexane (−30 °C, overnight). Yield 195 mg (89%). ^{1}H NMR (C$_6$D$_6$, RT): δ 7.15 − 7.01 (6H), 4.97 (s, 1H, γ -CH), 3.92 (sept, 2H, CH(Me)$_2$), 3.30 (sept, 2H, CH(Me)$_2$), 1.61 (s, 6H, CH$_3$), 1.50 (d, 6H, CH(Me)$_2$), 1.31 (d, 6H, CH(Me)$_2$), 1.17 (d, 6H, CH(Me)$_2$), 1.00 (d, 6H, CH(Me)$_2$), 0.84 (s, 9H, ^{t}Bu). 1^{13}C NMR (C$_6$D$_6$, RT): δ 169.7, 145.9, 142.6, 142.5, 125.6, 123.6, 98.3, 30.8, 29.6, 28.0, 25.7, 25.0, 24.9, 23.7, 23.4. Elemental Anal. Calcd (found) for C$_{33}$H$_{50}$ClGaN$_2$: C, 68.34 (67.86); H, 8.69 (8.83); N, 4.83 (5.56)

Supporting Information Available: Crystallographic data files of the **1**−**6** in CIF format, temperature-depending NMR spectra of **1** and **2**, mercury plot and table with selected bond length and angles of **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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